

Crystal Structure of 1,1-Dibutyl-1,1-bis[(4-methyl-1-piperidiny)dithiocarbamato] Tin(IV)

Zia-ur-Rehman^a, S. Shahzadi^a, S. Ali^{a,*}, A. Badshah^a and G.-X. Jin^b

^aDepartment of Chemistry, Quaid-i-Azam University, Islamabad 45320 Pakistan

^bDepartment of Chemistry, Fudan University, Shanghai 200433 People's Republic of China

(Received 6 December 2005, Accepted 12 February 2006)

The dibutyltin(IV) complex of 4-methyl-1-piperidinedithioic acid has been synthesized and characterized by X-ray diffraction. It was found that tin atom has distorted tetragonal geometry with the space group P-1.

Key words: X-ray structure, Organotin(IV), Dithiocarbamate, Monodentate, Distorted tetragonal

INTRODUCTION

The complexing ability of dithiocarbamates (DTCs) with metals has been known for many years. DTC forms a chelate with metals through its two donor sulfur atoms [1]. DTCs have been used for analytical applications, especially for the separation and determination of metals as metal chelates in thin layer [2], liquid [3] and gas chromatography [4].

EXPERIMENTAL

Equipment

Melting points were determined in a capillary tube using electrothermal melting point apparatus model MP-D Mitamura Riken Kogyo (Japan) and are uncorrected. X-ray diffraction (XRD) data were collected on a Bruker SMART APEX CCD diffractometer (Madison, WI USA) equipped with a graphite monochromator. Infrared spectra were recorded in the range of 4000-400 cm⁻¹ using KBr pellets on a FTIR spectrophotometer (Bio-Rad, Cambridge, MA, USA). Elemental analyses for carbon, hydrogen, nitrogen and sulfur were performed using

a Perkin Elmer model 2400 analyzer.

Chemicals

Analytical grade dibutyltin dichloride and 4-methylpiperidine were procured from Aldrich Chemical Company (Milwaukee, WI, USA) whereas CS₂ was purchased from Riedel-de Haën (Seelze, Germany).

Preparation of 1,1-Dibutyl-1,1-bis[(4-methyl-1-piperidiny)dithiocarbamato]tin(IV)

The reported complex (Fig. 1) was prepared by stirring

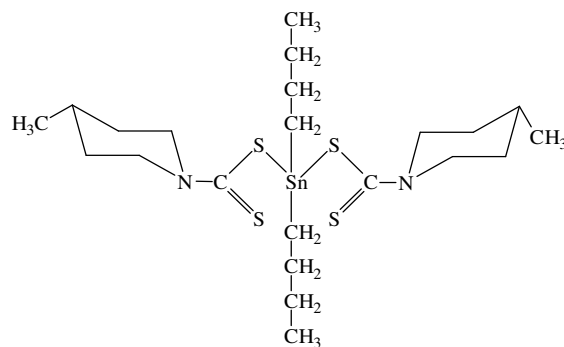


Fig. 1. Chemical structure of 1,1-dibutyl-1,1-bis[(4-methyl-1-piperidiny)dithiocarbamato]tin(IV).

*Corresponding author. E-mail: drsa54@yahoo.com

equimolar quantities of 4-methylpiperidine and carbon disulphide at room temperature in methanol. After stirring for 2 h, equimolar amounts of Bu_2SnCl_2 dissolved in methanol was added dropwise to the reaction mixture in a round-bottom two-necked flask. This mixture was stirred vigorously for 3 h. The solid residue thus obtained was recrystallized from chloroform to yield colorless crystals. M.p.: 65-66 °C. Analysis Calcd.: for $\text{C}_{22}\text{H}_{42}\text{N}_2\text{S}_4\text{Sn}$: C, 45.43; H, 7.22; N, 4.81; S, 22.03. Found: C, 45.49; H, 7.29; N, 4.91; S, 22.13 (%). IR (KBr, cm^{-1}), 446 v (Sn-S), 561 v (Sn-C), 962, 960 v (CS_2).

RESULTS AND DISCUSSION

The crystal structure of the reported compound has one molecule in the asymmetric unit. It can be seen that the tin atom has a coordination number of four. The 4-methylpiperidine dithiocarbamates bond to the Sn atom through sulfur atoms (1) and (3), and Sn-S bond distances are

2.534 (12) and 2.536 (11) Å. The two carbamates are monodentate, coordinating to the Sn atom through S(1) and S(3). The bond distances of sulfur atoms (2) and (4) with Sn are 2.918 (14) and 2.919 (13) Å, which are too long to be strong covalent bonds. However, these Sn-S distances are shorter than the sum of the van der Waals radii for these atoms [5]; thus, these bonds may be considered weak. We think there are two important reasons for this: First, the strong electron-withdrawing nature of CH_3 decreases the electron density on the S atom of $\text{C}=\text{S}$ and reduces its ability to coordinate to the tin atom. Second, the steric interaction of the two bulky butyl groups and four-membered chelating ring may prevent the formation of the Sn(1)-S(2) and Sn(1)-S(4) bonds.

The C(15)-Sn-C(19) linkage is not linear, having an angle of $135.3 (16)^\circ$, which is much larger than the value expected for a regular tetrahedron. This coordination geometry is best described as distorted tetragonal. Another important distortion is caused by the asymmetric Sn-S bond lengths. Therefore, the

Table 1. Crystal Data of 1,1-Dibutyl-1,1-bis[(4-methyl-1-piperidinyl)dithiocarbamato]tin(IV)

Empirical formula	$\text{C}_{22}\text{H}_{42}\text{N}_2\text{S}_4\text{Sn}$	
Formula weight	581.51	
Temperature	293 (2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.596 (4) Å	$\alpha(^\circ) = 112.991 (5)^\circ$
	b = 12.843 (6) Å	$\beta(^\circ) = 103.817 (6)^\circ$
	c = 13.276 (6) Å	$\gamma(^\circ) = 91.323 (6)^\circ$
Volume	1450.1 (11) Å ³	
Z	2	
D_{calc}	1.332 g cm ⁻³	
F(000)	604	
Crystal size	0.16 × 0.12 × 0.10 mm ⁻³	
Theta range for data collection	26.509 to 2.123°	
Index ranges	-11 ≤ h ≤ 10, -15 ≤ k ≤ 14, -6 ≤ l ≤ 15	
Reflections collected	5039	
Independent reflections	4126 [R(int) = 0.0248]	
Refinement method	Full-matrix Least-squares on F ²	
Data/restraints/parameters	5039/0/262	
Goodness-of-fit on F ²	1.02	
Final R indices [I > 2σ(I)]	R ₁ = 0.033, wR ₂ = 0.082	
R indices (all data)	R ₁ = 0.046, wR ₂ = 0.090	

Crystal Structure

Table 2. Selected Bond Lengths [Å] and Angles [°]

Sn(1)-C(15)	2.137 (4)	C(15)-Sn(1)-C(19)	135.35 (16)
Sn(1)-C(19)	2.143 (4)	C(15)-Sn(1)-S(1)	104.02 (12)
Sn(1)-S(1)	2.5347 (12)	C(19)-Sn(1)-S(1)	107.95 (11)
Sn(1)-S(3)	2.5362 (11)	C(15)-Sn(1)-S(3)	107.54 (13)
N(1)-C(1)	1.329 (4)	C(19)-Sn(1)-S(3)	106.55 (11)
N(1)-C(13)	1.461 (5)	C(1)-S(1)-Sn(1)	95.31 (12)
N(1)-C(9)	1.468 (5)	C(2)-S(3)-Sn(1)	93.23 (12)
S(1)-C(1)	1.750 (3)	N(1)-C(1)-S(1)	118.4 (3)
S(3)-C(2)	1.747 (3)	C(14)-C(11)-C(10)	112.2 (4)
C(4)-C(5)	1.527 (6)	C(17)-C(16)-C(15)	117.1 (6)
C(10)-C(11)	1.525 (6)	C(20)-C(19)-Sn(1)	112.1 (3)

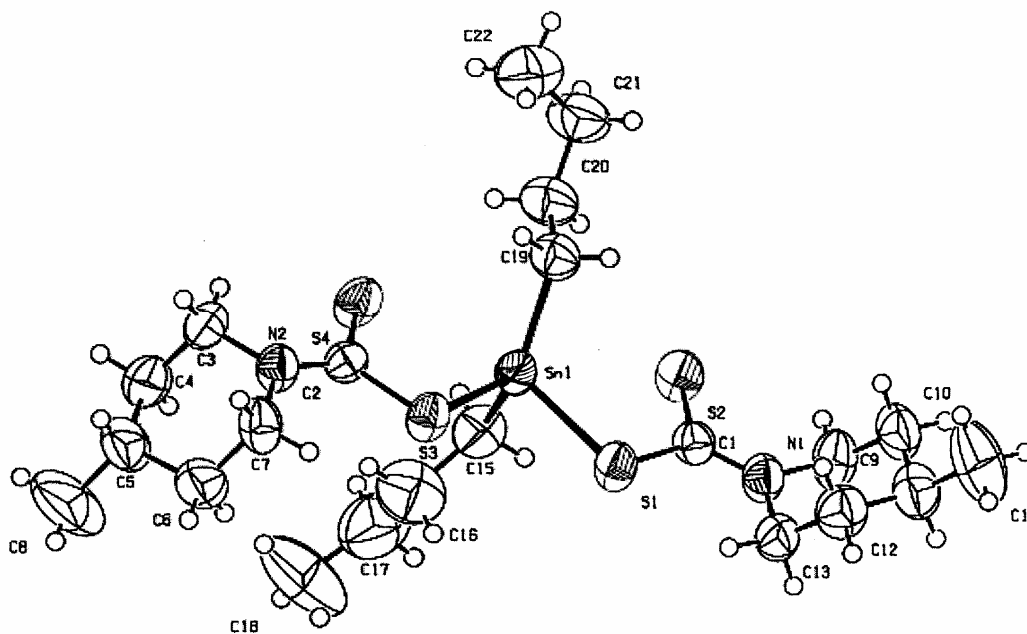


Fig. 2. ORTEP drawing of 1,1-dibutyl-1,1-bis[(4-methyl-1-piperidyl)dithiocarbamato]tin(IV) with atomic numbering scheme.

angle S(1)-Sn(1)-S(3) of 83.03 (14)°, is not consistent with true tetrahedral geometry, but instead with distorted tetragonal geometry. As a result, the Sn atom in **1** exists in a distorted tetragonal geometry in which the basal plane is defined by four S atoms, and the axial positions are occupied by two butyl substituents.

The crystal data is given in Table 1. Selected bond distances and angles are given in Table 2. XRD data were collected at room temperature using a Bruker Smart APEX CCD diffractometer. The data collected was reduced using SAINT [6] and an empirical absorption correction was performed using SHELX-97 [7].

The structure was solved by direct methods and refined with anisotropic displacement parameters for all non-hydrogen atoms by full-matrix least-squares using the SHELX-97 Package for PC [7]. An ORTEP [8] drawing with atomic numbering is shown in Fig.2.

Supplementary Material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 253345 for the reported complex. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

ACKNOWLEDGMENTS

The financial support for this work was provided by

Quaid-i-Azam University, Islamabad.

REFERENCES

- [1] A. Hulanicki, *Talanta* 14 (1967) 1371.
- [2] K.W. Weissmahr, L. Houghton, D.L. Sedlak, *Anal. Chem.* 70 (1998) 4800.
- [3] M.L. Riekkola, T. Pakkanen, L. Niinisto, *Acta. Chim. Scand.* 37 (1983) 807.
- [4] I.M. Pannacciulli, R.A. Lerza, G.U. Bogliolo, M.P. Mancoboni, *Brit. J. Cancer.* 59 (1989) 371.
- [5] A. Bondi, *J. Phys. Chem.* 68 (1964) 441.
- [6] Bruker, SADABS, SAINT and SMART, 2002, Bruker AXS Inc., Madison, Wisconsin, USA.
- [7] G.M. Sheldrick, SHELXL-97, 1997, University of Gottingen, Germany.
- [8] C.K. Johnson, ORTEP II. Report ORNL-5138, 1976, Oak Ridge National Laboratory, Tennessee, USA.